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PROTECTIVE FILM FOR OPTICAL RECORDING MEDIUM AND OPTICAL  
RECORDING MEDIUM USING IT

[光記録媒体用保護膜とそれを用いた光記録媒体]

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Specification

1. [Title of the invention]

Protective layer for optical recording medium and optical recording medium using it

2. [Scope of the patent claims]

(1) The protective film is made of silicon oxynitride provided at least on one side of the recording layer in the optical recording medium, and regarding the triangle coordinate wherein its atomic number ratio has  $(\text{Si}_{100}\text{N}_0\text{O}_0)$ ,  $(\text{Si}_0\text{N}_{100}\text{O}_0)$  and  $(\text{Si}_0\text{N}_0\text{O}_{100})$  as their vertices, the characteristics of protective layer for optical recording medium is that the inner side region is expressed by the triangle that connect each point of A( $\text{Si}_{60}\text{N}_0\text{O}_{40}$ ), B( $\text{Si}_{33}\text{N}_0\text{O}_{66}$ ) and C  $\text{Si}_{39.1}\text{N}_{34.1}\text{O}_{26.1}$  by successive line portions, and in its microscopic film structure, the concentration of the grain structure surrounded by the grain boundary is 10 pieces per  $1\ \mu\text{m}^2$ .

(2) The protective layer for optical recording medium constituted by the layer made of the protective layer described in claim item 1 and the layer that is provided at the uppermost layer of the optical recording medium and is made of the layer consisting of UV beams cured resin whose cured shrinkage rate is 5~10%.

(3) The characteristics of Optical recording medium is that at least on one surface of the recording layer there is the protective layer described in the claim item 1.

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<sup>1</sup> Numbers in the margin indicate pagination in the foreign text.

(4) The characteristics of the optical recording medium are that it has the protective layer described in claim item 2.

3. [Detailed explanation of the invention]

[Utilized field in industry]

The present invention relates to the novel protective film for optical recording medium and the optical recording medium equipped with it in the structure. Furthermore, in more detail, the present invention relates to the protective layer for optical recording medium wherein optical recording medium that can be used under the harsh environment of high temperature and high humidity is provided, hence, it has a high mechanical strength and peeling and cracking are controlled from being generated, and the protective layer for optical recording medium equipped with it.

[Prior arts]

In the recent years, the optical recording medium can record with high concentration and can be accessed by high speed. Because it has high reliability and was a non contact type, it has been getting attention as the carrier of the central role of the recording medium in the sophisticated information society and the research has been going on constructively. Regarding this recording medium, /2 there are three types such as reproduction specializing type such as compact disks and CD-ROM, multi secession drive type that can record and reproduce the information as document and image films and the like, and re-writable type that can record and erase and reproduce represented by floppy disks, and all has been in market for commercialization.

By the way, regarding the optical recording medium that are aforementioned multi session or rewritable type, recording layer is provided on the substrate, and regarding recording layer, various ones with different recording method principle and mode have been developed. For instance, in case of multi session type, the open pore method that uses the organic pigment such as naphtho quinon and the like and alloys and oxide that use Se, Te and the like that are chalcogen as the main, or phase change type that uses the alloys and the like that has Ga, Ge, Se, In, Sn, Sb, Te, Pb, Bi and the like as the main have been developed. And regarding re-writable type, other than aforementioned phase change method, the optical magnetic method has been developed by vertical magnetized thin film that has as the main the alloy with transition metal heavy rare earth type and garnet.

By the way, as the photo sensitive material used for these recording layer, many are chemically unstable, in addition, since it is used for thin films, it is easily oxidized by the oxygen in the air and by water, this relates to the performance of recording and reproduction, hence, as time passes, reliability reduction is inevitable.

In order to solve these defects, protective layer has been provided on the top or bottom of both sides of the recording layer in optical recording medium normally. As its protective layer, in general, it is known that using dielectric thin film is advantageous wherein barrier characteristics is superior in preventing the oxygen or water from penetrating effectively and the substance itself is

chemically stable, and as its material, for instance, magnesium, silicon, aluminum that are oxide, and nitride, oxynitride and their composites, sulfide of the metal such as zinc and selenium compound, furthermore their mixture have been attempted to be used.

However, regarding the protective films made of these materials, the defects are that it has poor sealability with the substrate, thus, peeling is liable to be produced, in addition, it is brittle and cracking is liable to be produced. If such peeling and cracking are produced, the reflectivity of the part decreased, and causes errors, and also oxygen and water invades the recording layer, thus causing the corrosion. Particularly, in case optical recording medium is used under the high temperature and high humidity environment, the problems arise wherein the warping occurs by the difference of expansion rate of the constituent elements of said medium, that is, substrate, protective layer, recording layer and residual stress induces the peeling between the protective layer and the substrate and the cracking of the protective layer, thus, the utilization range of optical recording medium is restricted inevitably.

Among aforementioned material, silicon oxynitride is comparatively peeling cracking free material, however, the protective layer comprising only this is still insufficient, hence, a method is proposed (Japan Published Patent Tokkai Sh63-166046 Gazette) wherein combining with silicon oxide, two layers are made. However, even using such a method, peel resistance characteristics and cracking resistance characteristics are not necessarily sufficient, additionally, in order to make two layers, production

process is increased by one process, thus making industrial execution unadvantageous.

[Problems the present invention attempts to solve]

The present invention attempts to overcome the defects of the traditional protective layer used for such optical recording medium, and the purpose of the present invention is to provide the protective layer for optical recording medium wherein the protective films are provided that has high mechanical strength and peeling and cracking are not easily produced, and by using this, it can be used under the harsh environment of high temperature and high humidity.

[Means to solve the problems]

These inventors were engaged in various researches regarding protective layer for optical recording medium, as its result, they found that, made of the oxynitride of the silicon in which atomic number ratio of silicon, nitrogen and oxygen is within a specified range, and also using the protective layer having a specified film structure, or using jointly with the layer provided at the topmost layer along with this, and also, made of the UV beams cured resin that has a specified cured shrinkage rate, the purpose is attained.

Based on this knowledge, they completed the present invention.

That is, the present invention provides the optical recording medium wherein the protective film is made of silicon oxynitride provided at least on one side of the recording layer in the optical recording medium, and regarding the triangle coordinate wherein its atomic number ratio has  $(SI_{100} N_0 O_0)$ ,  $(SI_0 N_{100} O_0)$  and  $(SI_0 N_0 O_{100})$  as their vertices, the characteristics of protective layer /3

for optical recording medium is that the inner side region is expressed by the triangle that connect each point of A( $\text{Si}_{60} \text{N}_0 \text{O}_{40}$ ), B( $\text{Si}_{33} \text{N}_0 \text{O}_{66}$ ) and C ( $\text{Si}_{39.1} \text{N}_{34.1} \text{O}_{26.1}$ ) by successive line portions, and in its microscopic film structure, the concentration of the grain structure surrounded by the grain boundary is 10 pieces per  $1 \mu\text{m}^2$ .

And the protective layer for optical recording medium characterized as above or the layer made of the protective layer described as above, and the layer that is provided at the uppermost layer of the optical recording medium and is made of the layer consisting of UV beams cured resin whose cured shrinkage rate is 5~10% and the optical recording medium that has these protective layers are provided.

The following will explain the present invention in detail.

Regarding the silicon oxynitride in the protective layer of the present invention, it is necessary that the atomic number ratio of silicon, nitrogen and oxygen, in the triangle coordinate with the vertex of ( $\text{Si}_{100} \text{N}_0 \text{O}_0$ ), ( $\text{Si}_0 \text{N}_{100} \text{O}_0$ ) and ( $\text{Si}_0 \text{N}_0 \text{O}_{100}$ ), has the composition in the region surrounded by the line that connects 3 points in aforementioned A, B, and c.

In general, silicon oxynitride has the characteristics wherein within comparatively wide composition range, it is superior in the barrier characteristics against the water and oxygen, chemical stability under the high temperature and high humidity environment, and mechanical strength under a harsh using environment, however, in the present invention, in aforementioned triangle coordinate,



it is necessary that the composition range be used that is represented by Si side from the line portion that connects  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  that are two stoichiometric compound. If this composition range is deviated, it means that excess oxygen and nitrogen exist in the film, and these disperse gradually into the recording layer, it tends to lose the stability of the recording layer. And it is necessary that this atomic number ratio against oxygen be less than 1.5, and if this atomic number ratio is 1.5 or more, it ends up as the oxygen relatively lacking in the oxygen, and in such composition, unreacted silicon bonds with the oxygen as time passes, the volume increases, hence, compression stress is produced, thus, causing the peeling of the protective layer.

Figure 1 is the triangle coordinate graph showing the atomic number ratio of silicon, nitrogen and oxygen, however, in the present invention, it is necessary that silicon oxynitride be used that has the composition of the region inside from the triangle that sequentially connects the line portion of 3 points A( $\text{Si}_{60} \text{N}_0 \text{O}_{40}$ ), B ( $\text{Si}_{33} \text{N}_0 \text{O}_{66}$ ), C ( $\text{Si}_{39.1} \text{N}_{34.1} \text{O}_{26.1}$ ).

Furthermore, in the protective layer of the present invention, it is necessary that the composition of the silicon oxynitride to be used meets the aforementioned condition but also, in the microscopic film structure, the concentration of the grain structure surrounded by the grain boundary be 10 pieces per  $1\mu\text{m}^2$ . The grain structure referred to here denotes structure unit of the film surrounded by grain boundary completely.

If the production method the film is unsuitable, many of above described structure unit in the film are produced, it ends up containing many grain boundaries per unit volume. By improving the film making method, the grain boundary that divides aforementioned grain structure become gradually discontinuous, separate grain structure get linked together, its entire number decreases. When this makes more progress, the continuous grain boundary that completely surrounds one grain structure does not exist any more, presenting the structure as though entire film is one grain structure. Ideally, it is desired that there is no continuous grain boundary that forms the grain structure inside the film structure, the whole makes a uniform film structure, however, in order to attain the purpose of the present invention, it is acceptable if the concentration of the grain structure of the protective layer is 10 pieces per  $1\mu\text{m}$  or less. In the regular thin film making method, microscopic film structure in the protective film becomes island shaped easily and it is speculated that the cracking is produced from the grain boundary between the structures. Hence, as described before, the concentration of the grain structure is made 10 pieces per  $1\mu\text{m}^2$  or less, thereby, cracking is not easily produced in the protective layer of the present invention, and mechanical strength is made high.

As the method to form the protective layer of the present invention, well known methods such as for instance, sputtering method, vapor evaporation method, CVD method, ion plating method and the like can be used. However, in order to sufficiently

demonstrate the effect of the present invention, sputtering method is favorable. And by sputtering method, in order to obtain the oxynitride of the desired composition, it is advantageous to form the film by reactive sputtering method.

The size of the grain structure of the thin film formed by such sputtering method depends on gas pressure and the power mainly, and if the growth speeds of the structure during thin film formation is slow compared with the nucleus formation method, grain structure become small, and desired protective film is not obtained. Hence, it is effective if the power of the sputter is raised or the pressure is decreased, the rate is raised,

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however, controlling method of grain structure by power can produce an unfavorable situation such as raising the substrate temperature, and hence, gas pressure controlling method is advantageous.

Regarding the specific value of gas pressure, it varies by the gas pressure, it can not be fixed, however, if it is normally 0.8 Pa or less, preferably 0.5Pa or less, desired film structure can be obtained.

And, as a target, silicon compound or silicon element can be used, however; in general, it is easy to form the desired film by silicon compound, hence more advantageous. In case silicon element is used, reaction and structure growth make progress on the substrate in parallel, hence, nucleus formation speed slows down relatively, and it is necessary to narrow down the range of the sputtering condition (particularly the gas pressure) to form the desired grain

structure, hence, not preferred. In case this method is adopted, it is desired that the partial pressure of the reaction gas is made excessive and the Si targeting surface be formed into the compound.

And, according to the sputtering method by argon, oxygen and mixed gas wherein  $\text{Si}_2\text{N}_4$  target is used and flow amount ratio is adjusted, the film ends up with insufficient nitrogen due to the composition of the oxynitride of the present invention; however, in this case, it is good if nitrogen gas is mixed.

In order to confirm whether or not the protective layer thus formed has the desired size of the grain structure; it is good to use the transmission type electron microscope that has the resolution capability of submicron order. According to this method, it can obtain the resolution capability of about 1nm normally, or more. The grain structure described in the present invention is divided by the grain boundary with clear contrasts, hence, its number can be found easily. Regarding the protective layer formed by sputtering method, when the gas pressure during forming is reduced, the contrast of the grain boundary becomes gradually smaller, and one can notice that the grain structure and grain structure are connected continuously.

In order to effectively prevent peeling and cracking which is the purpose of the present invention, it is effective if the protective layer is formed that is made of the UV beams cured resin on the topmost layer of the optical recording medium. In this case, it is necessary that the regarding protective layer from said UV beams cured resin, cured shrinkage rate is in 5~10% range. If the

cured shrinkage rate deviates from the aforementioned range, its effect is not sufficiently demonstrated. The reason is that the stress value necessary for controlling peeling and cracking is not suitable. That is, if the cured shrinkage rate of said UV beam cured resin is less than 5%, the stress for controlling peeling and cracking is not obtained, if it exceeds 10%, the stress is too high; it rather raises the possibility of inducing peeling and cracking.

The film thickness of said UV beam cured resin layer is selected in the range of 15~39 $\mu$ m normally. If this film thickness is less than 15 $\mu$ m, it is too thin, and stress adjustment by the cured shrinkage rate of said UV beam cured resin is difficult, and if it exceeds 30 $\mu$ m, optical polymerization reaction is likely to be insufficient.

IN the present invention, as the monomer of said UV beam cured resin used favorably, there is for instance, styrene, ethyl

acrylate, ethylene glycol diacrylate, ethylene glycol methacrylate, penta erythrytol acrylate, penta erythrytol methacrylate, penta erythrytol tetra acrylate, penta erythrytol tetra methacrylate, trimethylol propane triacrylate, trimethylol propane triemethacrylate, trimethylol propane diacrylate, trimethylol propane dimethyacrylate, and their derivatives and the like. One type of this monomer can be used or two or more types can be combined.

As the method to coat said UV beam cured resin monomer, well known methods, such as spin coating, gravia coating, spray coating, dipping and the like can be used. However from the stand point of productivity, spin coating method is particularly favorable.

It depends on improvement of mechanical strength of the protective layer formed like this, hence, optical recording medium provided with this protective layer has no particular restriction as to its method, type, and material. For instance as the type, any one of the reproduction specializing type, multi session type, rewritable type can be used. And as to the method, any one of open pore method, phase change method and optical magnetic method can be used, and as to the material, other than the metal such as aluminum that are generally used, any of chalcogen type alloy and oxide, rare earth type transition metal alloy, organic pigment and the like can be used.

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Furthermore, as to the type of substrate material, there is no particular restriction, for instance, any of glass, acrylic resin, polycarbonate resin epoxy resin and the like can be used, among them, the protective film of the present invention is particularly useful against the plastic substrate with large expansion rate under high temperature and high humidity.

In the present invention, the protective layer of the present invention made of the silicon oxynitride has been provided on the top or bottom of both sides of the recording layer in aforementioned optical recording medium. Furthermore, depending on the case, on the topmost layer of the optical recording medium, the protective film made of the UV beam cured resin of the present invention is provided, thus optical recording medium is obtained that can be used under high temperature and high humidity environment.

Next, according to the attached drawings, the optical recording medium of the present invention will be explained.

Figure 2 through figure 4 are the expanded cross section drawings showing each different structure example of optical recording medium, in figure 2, on substrate 1 is sequentially laminated interference layer 2, recording layer 3 and protective layer, thus forming four layered optical recording medium. And next, in figure 3, is formed the optical recording medium made of 5 layers where furthermore, reflective layer 5 is provided on protective layer 4. And in figure 4, on the above described reflective layer 5 is provided protective layer 6 made of UV beam cured resin, thus forming the optical recording medium made of six layers.

[Effects of the invention]

Protective layer for optical recording medium of the present invention provided at least on one side of the surface of the recording layer in the optical recording medium is made of silicon oxynitride, and by forming the film having the specified composition and microscopic film structure, it is superior in the barrier characteristics against the water and oxygen, chemical stability under the high temperature and high humidity environment, peeling and cracking are not easily generated.

The protective film of the present invention with such superior characteristics is provided at least on one side of the recording layer in the optical recording medium, thereby, said optical recording medium can be used under the high temperature and high

humidity harsh environment and is superior in the environment resistance characteristics.

Furthermore, on the topmost layer of this optical recording medium is provided the protective film made of UV beam cured resin with specified cured shrinkage rate, thereby, said optical recording medium is more superior in environment resistance characteristics.

[Embodied example 1]

On the polycarbonate substrate (1.2mm thick) with guide grooves of 130mm in diameter, an interference layer 2 made of 80nm thick  $\text{SiN}_x\text{O}_y$ , a recording layer 3 made of 80nm thick  $\text{Tb}_{20}\text{Fe}_{70}\text{Co}_{10}$  and a protective layer 4 made of 80nm thick  $\text{Si}_{45}\text{N}_{20}\text{O}_{35}$  are sequentially set up, thus making optical magnetic disk medium with the structure shown in figure 2. aforementioned recording layer was formed by alloy targeting DC magnetron spatter (gas pressure 0.4Pa, power 200W), a protective layer was formed by Si targeting reactive RF magnetron spatter (gas pressure 0.4Pa,  $\text{N}_2$  partial pressure 0.04 Pa,  $\text{O}_2$  partial pressure 0.05Pa, power 400W), the interference layer that combines a protective layer was formed by using Si target and setting up various film forming conditions. At this time, spatter gas was mixed gas of Ar,  $\text{N}_2$ ,  $\text{O}_2$  and gas partial pressure was adjusted so that the composition of the interference layer formed becomes  $\text{Si}_{45}\text{N}_{20}\text{O}_{35}$ .

Next, in order to evaluate the environmental resistance characteristics, using hot melt type adhesive agent, two sheets of these disks are pasted together, and stood still for 200 hours under the 90% RH accelerating life span testing environment.



And, separate from this, in order to observe the film structure of the interference layer, one is prepared in which only interference layer is formed on the aforementioned same substrate, and the grain structure was observed by the transmission type electron microscope (hereafter called TEM) with resolution capacity of 0.6nm. The device used was made by Hitachi H-500. In the first table, the relationship between film making condition and cracking occurrence is shown.

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[TABLE 1]

No.	Gas pressure (Pa)	Power (W)	Existence or non-existence of cracking occurrence
1	0.60	400	Yes
2	0.45	400	No
3	0.45	200	Yes
4	0.40	400	No
5	0.20	400	No

Under high gas pressure condition (No.1), many cracks were generated in the medium in 50~100 hours, no recording and reproduction were enabled.

In figure 5 and figure 7 are shown TEM pictures of film structure of the above described samples, in sample No. 1 in figure 5, many grain boundaries are clearly noticed, as against this, regarding the sample No. 5 in figure 6, there is only one grain structure inside the cross section of  $1\mu\text{m}^2$ , and it shows that there is no grain boundary and it is uniform. Furthermore, regarding the sample No. 3 in figure 7, grain boundary similar to No. 1 is noticed, how, continuous grain

boundary does not surround the grain structure, the number of grain structures inside the  $1\mu\text{m}^2$  is several.

According to the above described study, cracking occurrence can be prevented if grain structure completely surrounded by the grain boundary is limited to a several per  $1\mu\text{m}^2$  in cross section and in order to form the film with such a few grain boundary, it is effective to lower the gas pressure (according to the condition of this embodied example, it is 0.45Pa or less), one can tell. And in these TEM pictures, wavy denseness and lightness is seen, however, since the sample for observation is not completely flat, seeming contrast was added, and it has nothing to do with the grain boundary or grain structure of the present invention.

#### Embodied example 2

On the polycarbonate substrate (1.2mm thick) with guide grooves of 130mm in diameter, an interference layer 2 made of 120nm thick  $\text{SiN}_x\text{O}_y$ , a recording layer 3 made of 30nm thick  $\text{Tb}_{20}\text{Fe}_{70}\text{Co}_{10}$  and a protective layer 4 made of 35nm thick  $\text{Si}_{45}\text{N}_{20}\text{O}_{35}$ , and a reflective layer 5 made of aluminum with 40nm thick film are sequentially set up, thus making optical magnetic disk medium with the structure shown in figure 4.

aforementioned recording layer was formed by alloy targeting DC magnetron spatter (gas pressure 0.4Pa, power 200W), a protective layer was formed by Si targeting reactive RF magnetron spatter (gas pressure 0.4Pa,  $\text{N}_2$  partial pressure 0.04 Pa,  $\text{O}_2$  partial pressure 0.05Pa, power 400W), and the reflection layer was formed by Al

targeting RF magnetron spatter (gas pressure 0.4Pa, power 200W). The interference layer that combines a protective layer was formed by using Si targeting reactive spatter and Si<sub>3</sub>N<sub>4</sub> target, setting up various films forming condition. At this time, spatter gas was mixed gas of Ar, N<sub>2</sub>, O<sub>2</sub> and gas partial pressure was adjusted so that the composition of the interference layer formed becomes Si<sub>45</sub> N<sub>20</sub> O<sub>35</sub>.

Next, in order to evaluate the environmental resistance characteristics of the disk, using hot melt type adhesive agent, two sheets of these disks are pasted together, and stood still for 200 hours under the 90% RH accelerating life span testing environment at 80 deg C,

Table 2 shows the relationship of film making condition and the existence or non-existence of cracking occurrence.

[TABLE 2]

No.	target	Gas pressure (Pa)	existence or non-existence of cracking occurrence
6	Si	0.60	Yes
7	Si	0.45	No
8	Si	0.20	No
9	Si <sub>3</sub> N <sub>6</sub>	0.75	Yes
10	Ni <sub>3</sub> N <sub>6</sub>	0.65	No
11	Si <sub>3</sub> N <sub>6</sub>	0.60	No
12	Si <sub>3</sub> N <sub>6</sub>	0.50	no

Same as in embodied example 1, high gas pressure condition, that is, under the condition where many grain boundaries are noticed, many cracks developed in the medium from 50~100 hours, no recording and reproduction are enabled. The gas pressure for forming the film

with few grain boundary varies depending on whether the target is Si or Si<sub>3</sub>N<sub>6</sub>, and in case of the former, 0.45 Pa or less, in case of the latter, 0.65Pa or less is preferred.

#### Embodied example 3

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On the polycarbonate substrate (1.2mm thick) with guide grooved of 130 mm in diameter, the optical magnetic disk medium with the same structure as in embodied example 2 was formed. Among those, a recording layer was formed by the alloy targeting DC magnetron spatter (gas pressure 0.4Pa, power 200W), a protective layer was Si targeting reactive RF magnetron spatter (gas pressure 0.4Pa, N<sub>2</sub> partial pressure 0.04Pa, O<sub>2</sub> partial pressure 0.05Pa, power 400W), a reflection layer was formed by Al targeting RF magnetron spatter (gas pressure 0.4Pa, power 200W). The interference layer that combines the protective layer was formed by reactive sputtering Si<sub>3</sub>N<sub>4</sub> target with the mixed gas of Ar and N<sub>2</sub> and O<sub>2</sub> and the partial pressure of the gas were adjusted and ones with various compositions were made. The sputtering condition was fixed to gas pressure 0.4Pa and power 200W.

Next, in order to evaluate the environmental resistance characteristics of disks, using hot melt type adhesive agent, two sheets of these disks are pasted together, and stood still for 500 hours under the 90% RH accelerating life span testing environment.

And, separate from this, in order to observe the film structure of the interference layer, one is prepared in which only interference layer is formed on the aforementioned same substrate, and the grain

structure was observed by the transmission type electron microscope (hereafter called TEM). In the table 3, the relationship between film making condition and existence or non-existence of cracking occurrence are shown.

[TABLE 3]

No.	composition	Existence or non-existence of cracking occurrence	Existence or non-existence of peeling occurrence
13	$\text{Si}_{1.5} \text{N}_{1.0} \text{O}_{55.7}$	No	No
14	$\text{Si}_{1.0} \text{N}_{1.0} \text{O}_{1.0}$	No	No
15	$\text{Si}_{1.5} \text{N}_{1.5} \text{O}_{66.7}$	No	No
16	$\text{Si}_{1.5} \text{N}_{1.0} \text{O}_{28.7}$	No	Yes
17	$\text{Si}_{1.0} \text{N}_{1.5} \text{O}_{15.7}$	No	no
18	$\text{Si}_{1.5} \text{N}_{2.0} \text{O}_{26}$	No	yes

In this embodied example, even if 500 hours passed, no cracking was generating for any of the disks.

In figure 5 is shown the TEM pictures of the film structure of No. 17 in this example. As clarified by this picture in the figure, only one grain structure exists in the cross section of  $1\mu\text{m}^2$ , one can tell that there is no grain boundary and the film is uniform. However, regarding the triangle coordinate, one that are within the composition range expressed on Si side by the line portion that connects  $\text{SiO}_2$  and  $\text{Ni}_3\text{N}_4$  that are two stoichiometric compounds and also one wherein the atomic number ratio of the silicon against oxygen is 1.5 or more, as it passes 200 hours, the peeling was generated between the substrate and interference layer, recording and reproduction were disabled.

Due to the above described result, for any of the composition of this embodied examples, cracking is prevented by decreasing the grain boundary, however, in the composition that deviates from the range in figure 1, peeling occurs, and it interferes with the recording and reproduction. And, in TEM pictures in figure 5, wavy denseness and lightness are seen, however, this is same as in embodied example 1, this has nothing to do with grain boundary and grain structure that are talked about in the present invention.

#### Embodied example 4

On the polycarbonate substrate (1.2mm thick) with guide grooved of 86 mm in diameter, the optical magnetic disk medium with the same structure as in embodied example 2 was formed. Among those, a recording layer was formed by the alloy targeting DC magnetron spatter (gas pressure 0.4Pa, power 200W), a protective layer was formed by Si targeting reactive RF magnetron spatter (gas pressure 0.4Pa, N<sub>2</sub> partial pressure 0.04Pa, O<sub>2</sub> partial pressure 0.05Pa, power 400W), a reflective layer was formed by Al targeting RF magnetron spatter (gas pressure 0.4Pa, power 200W). The interference layer that combines the protective layer was formed by reactive sputtering Si<sub>3</sub>N<sub>4</sub> target with the mixed gas of Ar and N<sub>2</sub> and O<sub>2</sub>, and the partial pressure of the gas were adjusted so that composition became Si<sub>45</sub> N<sub>20</sub> O<sub>35</sub>. The sputtering condition was fixed to gas pressure 0.4Pa and power 200W.

As the topmost layer of this protective layer for optical recording medium, iso propane solution of penta erythritol trimethacrylate was spin coated, this was cured by UV beams, thus

making a protective layer. At this time, illumination intensity of UV beams and illumination hours were varied, and ones with various cured shrinkage rates were made. All the film thickness was made to be 20 $\mu$ m. Doing as above, the structure of the optical magnetic disk medium thus made are shown in figure 6.

Next, in order to evaluate the environmental resistance of the disk, they stood still for 2,000 hours under the 90% RH accelerating life span testing environment at 80 deg c. In this embodied example, disks were not pasted together, but had single plate structure. The result is shown in table 4.

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[TABLE 4]

No.	Cured shrinkage rate (%)	Existence or non-existence of cracking occurrence	Existence or non-existence of peeling occurrence
19	4.2	No	Yes
20	6.0	No	No
21	7.8	No	No
22	9.0	No	Yes
23	9.0	No	no

As clarified by this embodied example, by adding the protective layer made of UV beams cured resin on the topmost layer of the disk, even if it has only single plate structure, peeling and cracklings are controlled up to 2,000 hours, however, in case cured shrinkage rate of UV beam cured resin is 5.0% or less, peeling occurs, one can tell.

#### 4. [Simple explanation of the drawings]

Figure 1 is a triangle coordinates drawing showing the composition range of the protective layer for optical recording medium of the present invention

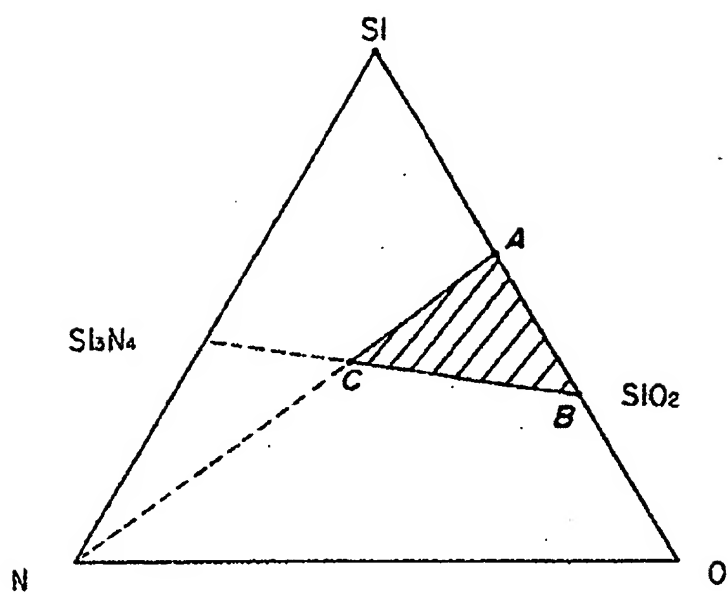
Figure 2 and figure 2 and figure 4 are cross section drawings respectively showing the different structure examples of protective layers for optical recording medium

Figure 5 and figure 7 are the electron microscope picture drawings showing the film structure of the protective film for optical recording medium respectively.

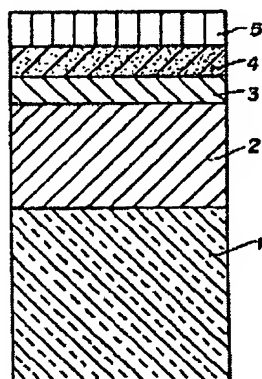
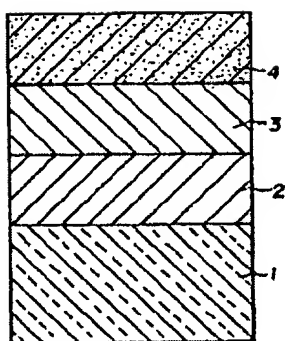
#### [Explanation of symbols]

1..substrate, 2. Interference layer, 3. Recording layer,  
4.. Protective layer, 5.Reflective layer, 6. I the protective layer  
made of UV beam cured resin





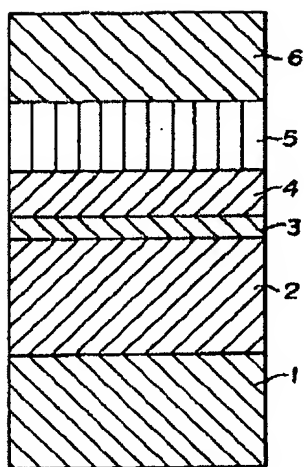
A(60.6 .0.0. 40.0)  
 B(33.3. 0.0. 66.7)  
 C(39.1. 34.8. 26.1)



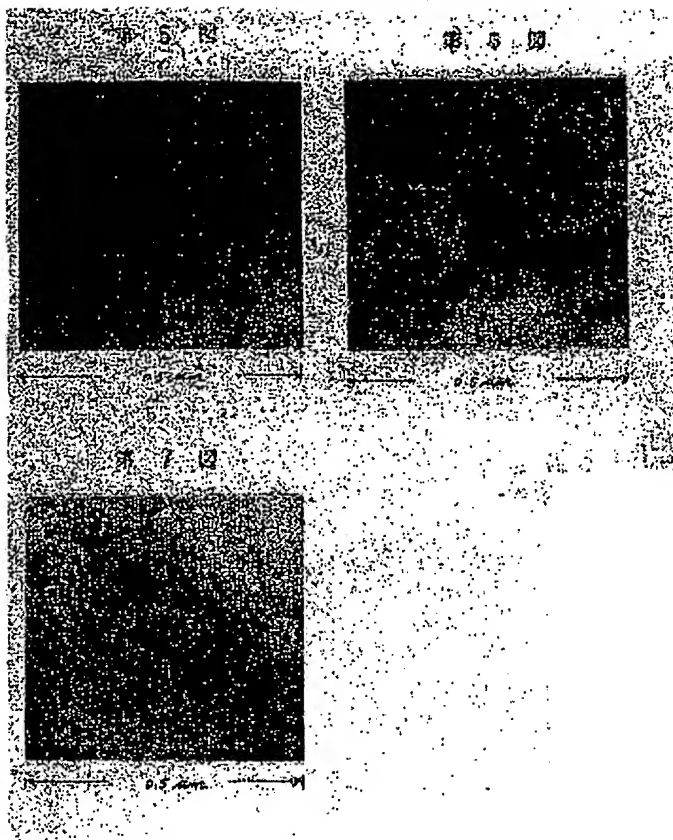
[Figure 2]

[Figure 3]

/9



[Figure 4]



[Figure 5], [Figure 6]

[Figure 7] together

The procedure correction document (method)

Dated July 2, 1990

To: Mr. Bun[illeg] Yoshida, Chief of the Japan Patent Agency

1. Display of the event

Patent Application #061236 dated 1990

2. Title of the invention

Protective layer for optical recording medium and optical recording medium using it

3. Correcting person

The relationship with the event: Patent applicant

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5. The date of correcting instruction June 19, 1990

(Mailing date: June 26, 1990)

6. The number of claims increased by the correction:

7. The correction target

The simple explanation column of the drawing of the  
specification

8. Correction content

(1). 6<sup>th</sup> row of the page 28 in the specification is changed from  
[the film structure of the protective layer for optical recording  
medium] to [the structure of the crystal of protective layer for  
optical recording medium]